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On minimal energies of acyclic conjugated molecules*

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Abstract. The energy of a graph is defined as the sum of the absolute values of the eigenvalues of the graph. Let Φ_n denote the class of trees with a perfect matching on n vertices. F. Zhang, H. Li [On acyclic conjugated molecules with minimal energies, Discrete Appl. Math. 92(1999) 71-84] have determined trees with minimal, second-minimal and third-minimal energies in Φ_n. In this paper, using the quasiordering relation, we discuss the trees in Φ_n having the fourth-, fifth- and sixth-minimal energies.

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1. Introduction

Let G be a graph on n vertices and $A(G)$ the adjacency matrix of G. The eigenvalues $\lambda_1, \ldots, \lambda_n$ of $A(G)$ are called the *eigenvalues* of G. Since $A(G)$ is real and symmetric, all eigenvalues of G are real. The *energy* of G, denoted by $E(G)$, is defined as

$$E(G) = \sum_{i=1}^{n} |\lambda_i| .$$

This concept was introduced by Gutman and is intensively studied in chemistry, since it can be used to approximate the total π-electron energy of a molecule (see, e.g, [6, 7]). There are a lot of results on $E(G)$ (e.g, see, [1, 2, 4-6, 8-13]).

For a graph G, let $m(G,k)$ be the number of k-matchings of G, $k \geqslant 1$, and, for convenience, define $m(G,0) = 1$, $m(G,k) = 0$ if $k < 0$. If G is an acyclic graph on n vertices, then the energy of G can be expressed as the Coulson integral [7]

$$E(G) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{dx}{x^2} \ln \left(1 + \sum_{k=1}^{\lfloor \frac{n}{2} \rfloor} m(G,k) x^{2k} \right) .$$

It is easy to see that $E(G)$ is a strictly monotonously increasing function of $m(G,k)$. This observation led Gutman [5] to define a *quasiordering* over the set of all acyclic graphs: If G_1, G_2 are two acyclic graphs, then

$$G_1 \succeq G_2 \Leftrightarrow m(G_1,k) \geqslant m(G_2,k) \text{ for all } k = 0, 1, \ldots \left\lfloor \frac{n}{2} \right\rfloor .$$

If neither $G_1 \preceq G_2$ nor $G_2 \preceq G_1$, then G_1 and G_2 are said *incomparable.* If $G_1 \succeq G_2$, and there is a j such that $m(G_1,j) > m(G_2,j)$, then we write $G_1 \succ G_2$. Therefore,

$$G_1 \succ G_2 \Rightarrow E(G_1) > E(G_2).$$

This increasing property of E has been successfully applied in the study of the extremal values of energy over some significant classes of graphs; see

[5,8,9,13,14,16-18]. Some most recent results along these lines are found in [10-12].

From the chemical point of view, it seems a more interesting problem to determine the extremal acyclic conjugated hydrocarbons (in the language of graph theory, trees with a perfect matching). In this case, denote by Φ_n the class of trees with a perfect matching on n vertices. Zhang and Li [15] characterized the trees in Φ_n having the minimal and the second-minimal energies (which solved two conjectures proposed by Gutman [4]), that is, $E(T) > E(E_n) > E(F_n)$ for any tree $T \in \Phi_n$ and $T \neq E_n, F_n$ (see Figure 1), and they also showed that the trees in Φ_n with the third-minimal energy

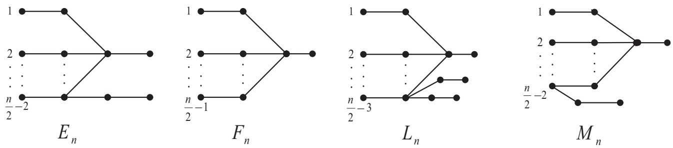

Figure 1: Graphs E_n, F_n, L_n and M_n.

is either L_n or M_n; see Figure 1. Furthermore, L_n and M_n are incomparable.

In this paper, as a continuance of [15], using the quasiordering relation $\prec$, we discuss the trees in Φ_n having the fourth-minimal energy.

2. Minimal energy of acyclic conjugated molecules

In this section, we shall discuss the trees with a perfect matching on n vertices having the fourth-, fifth- and sixth-minimal energies in Φ_n.

Let n be an even integer, and G be a graph of order $\frac{n}{2}$. Denote by G^* the graph obtained by attaching pendant edges to each vertex of G. In the following, let $\mathscr{T}_n$ denote the class of trees with n vertices.

The following method of counting the k-matchings of T is introduced by Zhang and Li [15]. Denote by $M(T)$ the perfect matching of a tree T. Let $m = |M(T)|$, $Q(T) = L(T) - M(T)$, where $L(T)$ is the edge set of T. Denote by $\hat{T}$ the graph induced by $Q(T)$, that is, $\hat{T} = T - M(T) - S$, where S is the set of singletons in $T - M(T)$. We call $\hat{T}$ the *capped graph* of T and T the *original graph* of $\hat{T}$. For each k-matching Ω of T, it is partitioned into two parts: $\Omega = R \cup S$, where $S \subset M(T)$ and R is a matching in $\hat{T}$. On the other hand, for any i-matching R of $\hat{T}$, and $k - i$ edges S of $M(T)$ not incident with R form a k-matching Ω of T with partition $\Omega = R \cup S$. And for all $T \in \Phi_n$, if $\hat{T}$ is connected, then any i-matching R in $\hat{T}$ is incident with exactly $2i$ edges in $M(T)$, hence, the number of k-matching in T including a certain i-matching R in $\hat{T}$ is $\binom{m-2i}{k-i}$. And these cover all the k-matchings in T as R goes over all matchings in $\hat{T}$. Therefore,

$$m(T, k) = \sum_{i=0}^{k} m(\hat{T}, i)\binom{m - 2i}{k - i}.$$

This fundamental principal is very useful for counting the k-matchings of T.

Lemma 2.1 ([5]). *$X_n \prec Y_n \prec Z_n \prec W_n \prec T \prec P_n$, and $E(X_n) < E(Y_n) < E(Z_n) < E(W_n) < E(T) < E(P_n)$ for any tree T and $T \neq X_n, Y_n, Z_n, W_n, P_n$ with n vertices, where X_n is the star $K_{1,n-1}, Y_n$ is the graph obtained by attaching a pendant edge to a pendant vertex of $K_{1,n-2}, Z_n$ by attaching two pendant edges to a pendant vertex of $K_{1,n-3}$, and W_n by attaching a P_3 to a pendant vertex of $K_{1,n-3}$.*

Lemma 2.2 ([15]). *The trees of the third smallest energy in Φ_n is either L_n or M_n, where L_n and M_n are in Figure 1.*

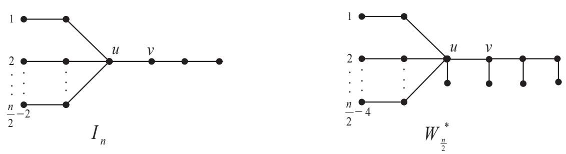

Figure 2: I_n and $W^*_{\frac{n}{2}}$

Lemma 2.3. *For any tree $T \in \Phi_n$ and $T \neq F_n, E_n, L_n$ and M_n, we have that either $E(T) \geqslant E(I_n)$ or $E(T) \geqslant E(W^*_{\frac{n}{2}})$. Furthermore, I_n and $W^*_{\frac{n}{2}}$ are incomparable.*

Proof. It is easy to see that $\hat{I_n} = K_{1,\frac{n}{2}-2} \cup P_2$. Note that $m(\hat{I_n}, 1) = \frac{n}{2} - 1$, $m(\hat{I_n}, 2) = \frac{n}{2} - 2$ and any 2-matching of $\hat{I_n}$ is incident with exactly three edges in $M(I_n)$, then

$$m(I_n, k) = \binom{m}{k} + \left(\frac{n}{2} - 1\right)\binom{m-2}{k-1} + \left(\frac{n}{2} - 2\right)\binom{m-3}{k-2}. \qquad (2.1)$$

It is easy to see that $\hat{W^*_{\frac{n}{2}}} = W_{\frac{n}{2}}$, and

$$m(W^*_{\frac{n}{2}}, k) = \binom{m}{k} + \left(\frac{n}{2} - 1\right)\binom{m-2}{k-1} + (n-7)\binom{m-4}{k-2}. \qquad (2.2)$$

Note that

$$m(I_n, k) - m(W^*_{\frac{n}{2}}, k) = (\frac{n}{2} - 2)\binom{m-3}{k-2} - (n-7)\binom{m-4}{k-2}.$$

When $n \leqslant 10$, $m(I_n, k) - m(W^*_{\frac{n}{2}}, k) \geqslant (5 - \frac{n}{2})\binom{m-4}{k-2} \geqslant 0$, i.e.,$I_n \succeq W^*_{\frac{n}{2}}$. When $n > 10$, $m(I_n, 2) - m(W^*_{\frac{n}{2}}, 2) < 0$, $m(I_n, m-1) - m(W^*_{\frac{n}{2}}, m-1) = \frac{n}{2} - 2 > 0$. This implies I_n and $W^*_{\frac{n}{2}}$ are incomparable.

Let $\Phi'_n = \{T | T \in \Phi_n$ and $\hat{T}$ is connected$\}$. For any tree $T \in \Phi'_n$ and $T \neq F_n, E_n$ and L_n, obviously $\hat{T} \neq \hat{F_n}, \hat{E_n}$ and $\hat{L_n}$. Note that $\hat{F_n} = X_{\frac{n}{2}}$, $\hat{J_n} = Y_{\frac{n}{2}}$, $\hat{L_n} = Z_{\frac{n}{2}}$. Combine with Lemma 2.1 and the fact that

$$m(T, k) = \sum_{i=0}^{k} m(\hat{T}, i)\binom{m-2i}{k-i}, \text{ for all } T \in \Phi'_n,$$

we have $E(W^*_{\frac{n}{2}}) \leqslant E(T)$ for all $T \in \Phi'_n$ and $T \neq F_n, E_n$ and L_n. By Lemma 2.1, for $T \in \mathscr{T}_{\frac{n}{2}}$, we have $E(T) = E(W_{\frac{n}{2}})$ if and only if $T = W_{\frac{n}{2}}$, hence, for $T \in \mathscr{T}_n \cap \Phi'_n$,

$$E(T) = E(W^*_{\frac{n}{2}}) \text{ if and only if } T = W^*_{\frac{n}{2}}.$$

Let $\Phi''_n = \{T | T \in \Phi_n$ and $\hat{T}$ is not connected$\}$. Note that $M_n \in \Phi''_n$ and M_n has the smallest energy in Φ''_n. We shall show that either $E(T) \geqslant E(I_n)$ or $E(T) \geqslant E(W^*_{\frac{n}{2}})$ for any tree $T \in \Phi''_n$ and $T \neq M_n$.

For all $T \in \Phi''_n$ and $T \neq M_n$, we distinguish the following two cases according to the components of T.

Case 1. Each components of $\hat{T}$ has at least two edges. Let the components of $\hat{T}$ be $\hat{T}_1, \cdots \hat{T}_c$, where c is the number of components in $\hat{T}$ and $||\hat{T}_i|| = a_i$, $i = 1, 2, \cdots c$. Since each edge in one component with an edge in another component form a 2-matching of $\hat{T}$, we have

$$m(\hat{T}, 2) \geqslant \sum_{1 \leqslant i < j \leqslant c} a_i a_j \geqslant a_1(a_2 + a_3 + \cdots + a_c) \geqslant 2\left(\frac{n}{2} - 3\right) = n - 6.$$

Note that $c \geqslant 2$ and in $\hat{T}$ the number of 2-matching which are incident with exactly three edges in $M(T)$ is no less than $c - 1$, then

$$\begin{aligned} m(T,k) &\geqslant \binom{m}{k} + \left(\frac{n}{2} - 1\right)\binom{m-2}{k-1} \\ &+ (n - 6 - (c-1))\binom{m-4}{k-2} + (c-1)\binom{m-3}{k-2} \\ &= \binom{m}{k} + \left(\frac{n}{2} - 1\right)\binom{m-2}{k-1} \\ &+ (n - c - 5)\binom{m-4}{k-2} + (c-1)\binom{m-3}{k-2} \\ &\geqslant \binom{m}{k} + \left(\frac{n}{2} - 1\right)\binom{m-2}{k-1} + (n-7)\binom{m-4}{k-2} + \binom{m-3}{k-2}. \end{aligned}$$

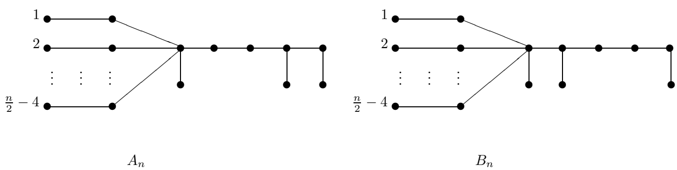

Figure 3: A_n and B_n

Let A_n be as in Figure 3. Note that $\hat{A}_n = K_{1,\frac{n}{2}-3} \cup P_3$, $m(\hat{A}_n, 1) = \frac{n}{2} - 1$, $m(\hat{A}_n, 2) = 2(\frac{n}{2} - 3) = n - 6$, $m(\hat{A}_n, k) = 0$ if $k \geqslant 3$ and only one 2-matching of all the 2-matchings in $\hat{A_n}$ is incident with three edges in $M(A_n)$. So

$$m(A_n,k) = \binom{m}{k} + \left(\frac{n}{2}-1\right)\binom{m-2}{k-1} + (n-7)\binom{m-4}{k-2} + \binom{m-3}{k-2}.$$

Therefore, $E(T) \geqslant E(A_n)$. By Eq.(2.2), we have $W^*_{\frac{n}{2}} \prec A_n$, hence $E(W^*_{\frac{n}{2}}) < E(A_n) \leqslant E(T)$.

Case 2. There exists a component T_1 of $\hat{T}$ which has only one edge. Let all the other components of $\hat{T}$ be T_2 (T_2 may be not connected), then $\hat{T} = T_1 \cup T_2$.

Subcase 2.1. T_2 is the star $K_{1,\frac{n}{2}-2}$. Since $T \neq M_n$ and $\hat{T} = K_{1,\frac{n}{2}-2} \cup P_2$, we have that $T = I_n$.

Subcase 2.2. T_2 is not the star $K_{1,\frac{n}{2}-2}$. If T_2 is not connected, we have $m(T_2,2) \geqslant \frac{n}{2}-3$; otherwise, by Lemma 2.1, $m(T_2,2) \geqslant m(Y_{\frac{n}{2}-1},2) = \frac{n}{2}-4$. Then w.l.o.g. we may assume $T_2 = Y_{\frac{n}{2}-1}$, i.e., $\hat{T} = Y_{\frac{n}{2}-1} \cup P_2$. Therefore, $m(\hat{T},1) = \frac{n}{2}-1$, $m(\hat{T},2) = n-6$ $m(\hat{T},3) = \frac{n}{2}-4$, and $m(\hat{T},4) = 0$ if $k \geqslant 4$.

Note that $\hat{T}$ has two components. Let the number of 2-matching in $\hat{T}$ which is incident with exactly three edges of $M(T)$ is x and the number of 3-matchings in $\hat{T}$ which is incident with exactly five edges of $M(T)$ is y, then

$$\begin{aligned} m(T,k) &= \binom{m}{k} + \left(\frac{n}{2}-1\right)\binom{m-2}{k-1} + (n-6-x)\binom{m-4}{k-2} + x\binom{m-3}{k-2} \\ &\quad + \left(\frac{n}{2}-4-y\right)\binom{m-6}{k-3} + y\binom{m-5}{k-3}. \end{aligned}$$

Since $x \geqslant 1$, $y \geqslant 1$ and $x = y = 1$ if $T = B_n$ (see Figure 5), we have

$$m(T,k) \geqslant m(B_n,k) \quad \text{and} \quad E(T) \geqslant E(B_n). \tag{2.3}$$

Aware of the fact that $m(B_n,k) = \binom{m}{k} + (\frac{n}{2}-1)\binom{m-2}{k-1} + (n-7)\binom{m-4}{k-2} + \binom{m-3}{k-2} + (\frac{n}{2}-5)\binom{m-6}{k-3} + \binom{m-5}{k-3}$. Then $B_n \succ W^*_{\frac{n}{2}}$ and $E(B_n) > E(W^*_{\frac{n}{2}})$. Together with Eq.(2.3), we have $E(T) \geqslant E(B_n) > E(W^*_{\frac{n}{2}})$. Therefore, our result follows easily. □

Note that $m(M_n,k) = \binom{m}{k} + (\frac{n}{2}-1)\binom{m-2}{k-1} + (\frac{n}{2}-3)\binom{m-4}{k-2} + \binom{m-3}{k-2}$. Combine with Eq.(2.1), we have that $M_n \prec I_n$, hence, $E(M_n) < E(I_n)$. It is easy to see that $E(L_n) < E(W^*_{\frac{n}{2}})$. Thus summarizing Lemmas 2.2 and 2.3, we arrived:

Theorem 2.4. *Let Φ_n denote the class of trees on n vertices which have a perfect matching.*

(i) *If L_n is the tree of the third smallest energy in Φ_n, then the tree of fourth smallest energy in Φ_n is either M_n or $W^*_{\frac{n}{2}}$.*

(ii) *If M_n is the tree of the third smallest energy in Φ_n, then the tree of fourth smallest energy in Φ_n is either L_n or I_n.*

Remark. In fact, by Lemmas 2.2 and 2.3 we can deduce that the set of trees with third-, fourth-, fifth- and sixth-minimal energies in Φ_n is just $\{L_n, M_n, I_n, W^*_{\frac{n}{2}}\}$, but unfortunately we can not determine which one in $\{L_n, M_n, I_n, W^*_{\frac{n}{2}}\}$ is the third, the fourth, etc. smallest energies in Φ_n. So it remains an open mathematical problem and is waiting for a satisfactory solution.

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